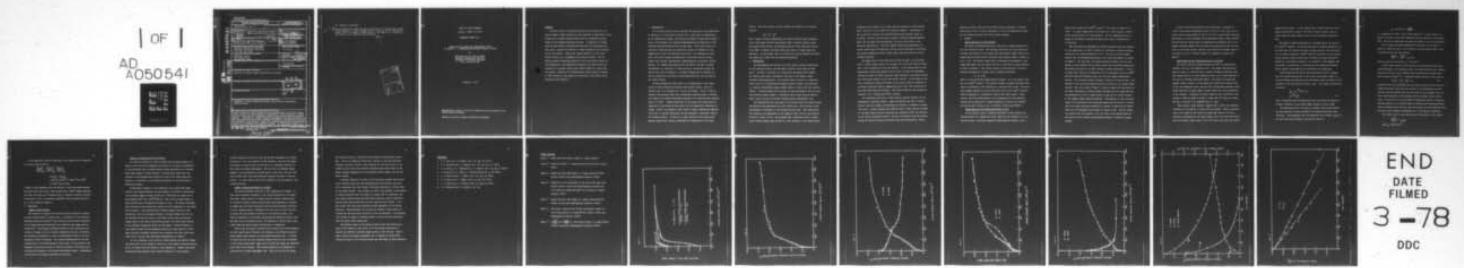


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20. Abstract (Continued)

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TECHNICAL REPORT NO. 5

INTERACTION OF OXYGEN WITH CARBONACEOUS LAYERS
ON Ni(110) I: DEHYDROGENATED ETHYLENE LAYERS AT T<300°C

by

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December 1, 1977

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ABSTRACT

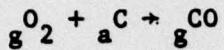
Previous studies of ethylene adsorption and decomposition on a Ni(110) single crystal surface have been extended to measurement of the interaction of oxygen molecular beams with the carbonaceous layers formed in the ethylene adsorption process. A combination of Auger electron spectrometric and modulated molecular beam techniques have been used to measure the kinetics of oxygen adsorption and CO production on the surface. Results for oxygen adsorption on the clean Ni(110) surface are in agreement with previous studies. For the surface formed by adsorbing ethylene on the clean nickel surface at room temperature, room temperature adsorption of oxygen results in formation of a surface layer of NiO without removal of carbon from the surface. Exposure of the ethyleneated nickel surface to oxygen at 260°C results in the removal of a fraction of the carbon, as CO, followed by NiO formation.

1. INTRODUCTION

In a previous report we have described the adsorption and decomposition of ethylene on a clean Ni(110) surface over a wide range of temperatures. At all temperatures studied, the reaction proceeded by dissociative adsorption of the ethylene, with complete dehydrogenation, and desorption of the resulting hydrogen molecules into the gas phase. The surface carbon concentration resulting from this adsorption process was dependent on the temperature at which the adsorption took place. For temperatures below 350°C, the final coverage corresponded to one carbon atom per surface nickel atom, probably representing a dehydrogenated C₂ molecular surface species. For temperatures between 350°C and 500°C, the final coverage corresponded to a monolayer of carbon having an interatomic spacing the same as the C-face of graphite. At higher temperatures no residual carbon was observed on the surface, indicating dissolution into the bulk of the nickel crystal.

We have extended the above study to an investigation of the interaction of these carbonaceous adlayers with gaseous oxygen. This is a reaction that is of interest for at least two reasons. First, it was observed in the previous study that a molecularly adsorbed phase of ethylene was formed on the surface following formation of the dissociatively adsorbed layer at T<350°C. Possible reactivity of this phase with oxygen would be indicated if this surface proved active for the dissociative adsorption of oxygen. Second, the graphitic layer formed at higher temperatures appeared to be inert to further adsorption, and may represent a "poisoned" state of the catalyst surface. If this is so, then reaction of this carbon with gaseous oxygen would provide a mechanism for regeneration of the clean

surface. With this in mind, we have observed the kinetics of the overall reaction



over a range of surface temperatures and initial surface carbon concentrations, using Auger electron spectrometry (AES) to measure surface carbon and oxygen concentrations, and modulated molecular beam relaxation spectroscopy (MMB) to measure scattered oxygen and product CO signal phase and amplitude. In the present report we discuss the results obtained at $T < 300^\circ\text{C}$. The results for $T > 300^\circ\text{C}$ will be presented separately.

2. EXPERIMENTAL

The measurements were carried out in the surface research system used for the previous studies, and described in detail in the report of that work.¹ In brief, it consists of a large metal ultrahigh vacuum chamber. The surface under study is mounted on the axis of the chamber using a universal positioning device. The reactant beam is formed by a supersonic nozzle source in a differentially-pumped auxiliary chamber, and modulated in a second differentially-pumped chamber before it enters the main reaction chamber. The main chamber also contains the mass spectrometer used to detect the scattered product signal, a cylindrical mirror Auger electron spectrometer, and an ion gun for surface cleaning between experimental runs.

Two modifications have been made to this system since the previous study. The detector mass spectrometer has been fitted with a new ion source, which uses magnetic confinement of the ionizing electron beam. This modification has resulted in an improvement of the signal-to-noise ratio of the detector by about a factor of five. The original beam modulation system, a large, multi-toothed chopper wheel driven by a motor external to the vacuum system,

developed uneven behavior due to wear, and was replaced by a much smaller wheel, driven by a motor inside the collimator chamber. Installation of this system has increased the available modulation frequency range to 15-300 Hz. We have also been able to obtain a Princeton Applied Research Model 2504 two-phase lock-in amplifier, for use at the output of the molecular beam detector. This unit permits simultaneous measurement of product signal phase and amplitude, and has proven invaluable in following the rapidly-changing CO product signal phase observed during the surface oxidation reaction.

The sample used in this study was the same one used in the previous work.¹ A nickel single crystal 2.5 cm long, 0.6 cm wide and 0.025 cm thick, with a (110) orientation on the flat surface. It was cleaned prior to the experimental studies and between runs by cycles of argon ion bombardment followed by anneal at 500°C, until the Auger spectrum of the crystal showed only those peaks typical of the clean nickel surface. In this phase of the work, carbonaceous layers were formed on the nickel surface by exposure to an ethylene molecular beam at temperatures below 350°C until saturation of the carbon AES signal was observed. The surface formed by this process is referred to as a "carburized Ni(110)" surface.

Two techniques were used to follow surface reaction kinetics for all experimental conditions studied. Auger spectroscopy was used to monitor surface carbon and oxygen concentrations as exposure to ethylene or oxygen took place. Previous studies have indicated that in this case the presence of the Auger primary electron beam does not observably affect the kinetics of the surface processes involved. The flux of molecules from the surface during the reaction process was measured mass spectrometrically, using a

modulated reactant beam and the two-phase lock-in amplifier at the mass spectrometer output to obtain information on both the magnitude and phase of the scattered reactant and product species signals.

3. RESULTS

Oxygen Adsorption on Clean Nickel

The initial measurement made was of the rate of oxygen adsorption on the clean Ni(110) surface. The sticking coefficient for this process was obtained from analysis of the oxygen mass spectrometer signal observed for oxygen beam scattering from an initially clean surface, shown in Figure 1a, as $S_0 = 0.78$. The overall uptake rate, as obtained by measurement of the oxygen AES signal from the nickel surface as a function of oxygen exposure is shown in Figure 2. The initial process is characterized by the dissociative adsorption of oxygen, with a sticking coefficient

$$S = S_0 (1-\theta)$$

where θ is the fractional oxygen adatom coverage, $\theta=1$ at an oxygen coverage of $\sim 5.5 \times 10^{14}$ atom/cm². The further increase in oxygen AES beyond this point is attributed to the formation of a surface layer of NiO. The saturation oxygen coverage for this process was found to be 2.4×10^{15} atom/cm², which corresponds to 3 monolayers of NiO on the (110) surface. These results, and this interpretation, are in agreement both with previous studies in the laboratory of oxygen adsorption on Ni(111) and Ni(100)² and the results of Norton et al. on Ni(110), Ni(111) and Ni(100).³

Oxygen Reaction with Carburized Ni(110) at 20°C

In the previous study of ethylene adsorption on this surface, the observed result for temperatures below $\sim 350^\circ\text{C}$ was the formation of a carbonaceous layer, containing completely dehydrogenated ethylene, with a

carbon atom coverage of $\sim 1.4 \times 10^{15}$ atom/cm². This layer is stable up to $\sim 350^\circ\text{C}$. At higher temperatures it transforms to a layer having a carbon-carbon spacing typical of C-face graphite. The low temperature layer is capable of molecularly adsorbing ethylene with a heat of adsorption of ~ 12 Kcal/mol.

Mass spectrometric measurement of oxygen scattering from this surface at room temperature, as shown in Figure 1b, indicated an initial sticking coefficient for oxygen adsorption of ~ 0.2 . The rate of surface oxygen buildup, and the accompanying decrease in the carbon AES signal, are shown in Figure 3. For this case, the oxygen adsorption kinetic curve is very similar to that observed for the clean surface case, differing primarily in the absolute rate, due to the lower initial sticking coefficient. In both of these cases, there is an inflection point in the uptake curve at $\sim 6 \times 10^{14}$ atom/cm², where NiO formation takes over from the oxygen chemisorption process. The saturation oxygen coverage is similar for both surfaces. The decrease in the carbon AES signal follows the increase in the oxygen signal closely. This can be seen in Figure 4, where we compare the attenuation of the carbon AES signal at various oxygen coverages with the oxygen AES signal multiplied by 0.433, a figure chosen to make the two curves coincide at the highest oxygen exposures measured. This behavior is what one would expect if the decrease in the carbon AES signal were due solely to scattering of the Auger electrons produced by a constant concentration of carbon atoms by an increasingly thick adlayer of oxygen or NiO. The only departure observed from this behavior is at the point in the process where the NiO layer is first forming and presumably growing to consume the oxygen adlayer.

A layer of NiO three monolayers thick would have a thickness of 4.43 \AA .³ The observed attenuation factor of 0.433 for this layer is consistent with an escape depth of $\sim 8\text{ \AA}$ for the 273 eV carbon Auger electrons. This figure is in good agreement with measurements made in other studies.⁴ The fact that the carbon signal is significantly attenuated even at low oxygen coverages suggests that the carbon atom adsorption sites lie very close to the nickel surface, possibly even within the outermost layer of the surface to form a "surface carbide" as suggested by McCarty and Madix.⁵

Oxygen Reaction with Carburized Ni(110) at T=260°C

The overall reaction sequence observed at 260°C is qualitatively different from the room temperature case. The oxygen scattering data, shown in Figure 1c, indicate both an initial sticking coefficient somewhat larger than for the room temperature case, and a slower approach to the very low sticking coefficient region. The carbon and oxygen AES signals, shown in Figure 5, both change more rapidly with exposure than in the room temperature case, and the close correspondence between carbon signal decrease and oxygen signal increase observed at room temperature is not observed. A desorbed CO product signal is also observed for the process at 260°C as shown in Figure 6, along with the carbon and oxygen AES data, replotted on an expanded scale vs. time.

These results, taken together, suggest that at least two processes contribute to the removal of carbon from the surface. This is indicated both by the breaks in the carbon and oxygen AES curves at $t=10$ sec., especially pronounced for the oxygen signal, and by the fact that the CO mass spectrometer signal drops to very low values long before the carbon

removal process stops. It also appears that at short times the rate of oxygen accumulation is equal to the rate of carbon removal, while at longer times the carbon removal rate is twice the oxygen accumulation rate.

The surface carbon concentration at the beginning of the reaction is 1.35×10^{15} atom/cm². In the previous study of ethylene adsorption, it was found that the initial adsorption process involved rapid adsorption up to a carbon coverage of 1.1×10^{15} atom/cm², equivalent to one surface carbon atom per surface nickel atom, followed by a slower adsorption process to a saturation coverage of ~ 1.4 atom/cm². This suggests that the surface, at saturation, is covered with two chemically different carbon species, which might react differently with oxygen gas.

We have analyzed the AES and mass spectrometer data by assuming that the reaction giving rise to the CO mass spectrometer signal is a reaction between the oxygen gas and the surface carbon in excess of that required to form the initial monolayer, $[_x C]$. This overall reaction can be written



This is consistent with the observation that the oxygen AES signal increase is identical to the carbon signal decrease at short times.

The desorption rate of CO from an otherwise clean nickel surface has been measured by Helms and Madix⁶ by a modulated molecular beam technique. They determined that the desorption rate constant, k_D (sec⁻¹) for the first-order desorption reaction was given by

$$k_D = 2 \times 10^{15} \exp\left(-\frac{33000}{RT}\right).$$

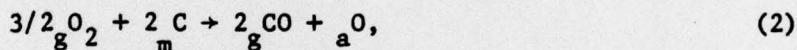
At a temperature of 260°C, this yields $k_D = 80 \text{ sec}^{-1}$, a value large compared to the rate of the carbon oxidation process observed in the present work. Thus the CO desorption rate does not appear to be rate controlling.

The CO signal decreases exponentially with time, as is shown in Figure 7a, where the log of the CO signal is plotted against time. This is consistent with the rate equation

$$\frac{d[\text{CO}]}{dt} = - \frac{d[\text{C}_x]}{dt} = k_x [\text{C}_x].$$

From the slope of this curve, $k_x = 0.04 \text{ sec}^{-1}$.

If the carbon removed by this process is subtracted from the total carbon AES signal, the remaining carbon, that associated with the original monolayer structure, $[\text{C}_m]$, likewise shows an exponential decrease with time as shown in Figure 7b. A possible overall reaction in this case is



consistent with the observation that the carbon removal rate is twice the oxygen accumulation rate when this process is the predominant reaction.

The fact that the reaction rate is first order in $[\text{C}_m]$ suggests that the rate controlling step in this process involves a single surface carbon atom. In this case it is not possible to definitely identify the gaseous reaction product, as no product signal is observed mass spectrometrically. This is probably due to the fact that the reaction is slow enough that the resulting product signal is demodulated to a very small ac amplitude.

The overall rate of this reaction can be described by the relation

$$\frac{d[\text{C}_m]}{dt} = - k_m [\text{C}_m]$$

with $k_m = 6 \times 10^{-3} \text{ sec}^{-1}$.

As an additional check on consistency, the initial rate of depletion of surface carbon should be

$$\begin{aligned}
 \left(\frac{d[\text{C}_a]}{dt} \right)_{t=0} &= \left(\frac{d[\text{C}_x]}{dt} \right)_{t=0} + \left(\frac{d[\text{C}_m]}{dt} \right)_{t=0} \\
 &= k_x [\text{C}]_0 + k_m [\text{C}]_0 \\
 &= (4 \times 10^{-2}) (2.5 \times 10^{15}) + (6 \times 10^{-3}) (1.1 \times 10^{15}) \\
 &= 1.7 \times 10^{13} \text{ molec/cm}^2 \text{ sec}
 \end{aligned}$$

a figure in good agreement with the AES data. Given the oxygen impingement rate used, this result, which implies that 1.7×10^{13} oxygen molecules per $\text{cm}^2 \text{ sec}$ are used up in forming CO and O_a , implies an initial sticking coefficient of 0.17, in reasonable agreement with the observed value of $S_o = 0.25$ as shown in Figure 1c.

4. DISCUSSION

Oxygen on Clean Ni(110)

The reaction of oxygen gas with various nickel surfaces is perhaps the most studied system in recent years. In addition to the previously mentioned adsorption studies^{2,3} this system has been studied extensively by low energy electron diffraction⁷ and reflection high energy electron diffraction.⁸ The sequence invariably observed is the dissociative adsorption of oxygen to form an ordered chemisorbed structure, followed by the nucleation and growth of a layer of NiO , generally found to be three monolayers of NiO in thickness. The results presented here do not add significantly to our understanding of this system. On the contrary, the agreement with previous studies is taken as evidence of the proper functioning and calibration of the present experimental system. Consequently no more will be said about this phase of the study.

Oxygen on Carburized Ni(110) at T=20°C

The apparent decrease in carbon coverage with increasing oxygen coverage in this case can be adequately accounted for in terms of attenuation of the AES signal from a constant surface carbon population by an increasingly thick oxygen or oxide overlayer. The only major effect that the presence of the adsorbed carbon appears to have on the oxygen adsorption process is a reduction in the sticking coefficient for the dissociative adsorption process.

As was shown in Figure 4, the attenuation of the carbon AES signal caused by the oxygen adsorption process appears to be directly proportional to the surface oxygen coverage, except for a discrepancy at oxygen coverages between 4×10^{14} and 1.2×10^{15} atom/cm². This is the coverage region in which the NiO layer is nucleated and begins to grow. The surface rearrangements involved in this process may account for the irregularity in the carbon AES attenuation. This proportionality between oxygen coverage and AES attenuation, even at low oxygen coverage, is strong evidence that the carbon adsorption sites lie closer to the nickel surface than the adsorbed oxygen atoms do, and that as the NiO layer grows, the carbon layer remains at the interface between the nickel and NiO phases. Further evidence for this position comes from the agreement between the escape depth for carbon Auger electrons calculated from this work, assuming a NiO layer three monolayers thick, and the value determined experimentally by others.⁴

It is not possible to tell from our studies whether the adsorbed oxygen and carbon react on the surface to form CO or other oxygen containing species, as CO, if formed, would not desorb at this temperature. Perhaps ultraviolet photoelectron spectroscopy could provide information on this question.

Another possibility would be to stop the present experiment at an oxygen coverage less than that required for NiO formation, then heat the sample and attempt to observe either CO evolution or a comparable reduction in both carbon and oxygen AES signals. The fact that the adsorbed oxygen appears to be incorporated in the NiO layer in this case, just as in the clean surface case, does argue indirectly against reactions to form CO, however. CO, once formed, would not be expected to give up oxygen to the forming NiO layer.

Oxygen on Carburized Ni(110) at T= 260°C

The reaction sequence observed at this temperature is complex. At least three processes contribute to the observed decrease in the carbon AES signal, namely reaction of oxygen with the "excess" surface carbon to form the CO gaseous product detected mass spectrometrically, reaction of oxygen with the carbon associated with the carbon monolayer structure to form a gaseous product, presumably CO or CO₂, but at a rate too slow to permit mass spectrometric detection of the reaction product, and finally attenuation of the signal associated with unreacted carbon by the NiO layer when it eventually forms. The formation of the NiO layer eventually stops the carbon removal process short of completion.

Both of the two removal reactions follow overall first order kinetics, but with significantly different rate constants, and different relationships between carbon removal rate and oxygen adsorption rate. It should be noted here that the rate constants obtained from the rate of decrease of the CO mass spectrometer signal and the carbon AES signal are "apparent" first order rate constants. They contain implicitly any dependence of reaction rate on oxygen impingement rate. They are thus not the values

that would be found in a molecular beam relaxation spectroscopic experiment. This is an important distinction, because at the beam modulation frequency used here, (40 Hz), rate constants for the unit process on the surface as low as the rate constants calculated here would result in the almost complete demodulation of the desorbed product signal, even for the faster process.

A question remains as to what is the distinction between what we have called "excess" carbon and that associated with the monolayer structure. It is conceivable that this "excess" represents adsorption at defect sites on the nickel surface. This, however, is felt to be unlikely, as the amount of carbon associated with this excess is roughly 20% of a monolayer, and the original nickel surface has been shown previously, both by AES and by helium atomic beam scattering to be very clean and well ordered. It is more likely that this excess population forms subsequent to the initial monolayer. This hypothesis can be tested by forming a carbon layer containing less than the amount required to form the monolayer, then exposing this surface to oxygen to determine whether the fast reaction associated with the excess carbon takes place.

The chemical nature of the species formed in the slow reaction process is also unknown at this point, as is the relative importance of gaseous and previously adsorbed oxygen species in the reaction. Experiments in which the oxygen impingement rate is changed or discontinued during the course of the reaction process may shed light on these questions.

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FIGURE CAPTIONS

Figure 1. Oxygen mass spectrometer signal vs. oxygen exposure

Figure 2. Oxygen AES signal vs. oxygen exposure-clean Ni(110) surface;
T=20°C.

Figure 3. Oxygen and carbon AES signals vs. oxygen exposure-Ni(110)
surface covered with dehydrogenated ethylene; T=20°C.

Figure 4. Comparison of the attenuation of the carbon AES signal from
Ni(110) surface covered with dehydrogenated ethylene with
0.433 times the oxygen AES signal as a function of oxygen
exposure; T=20°C.

Figure 5. Oxygen and carbon AES signals vs. oxygen exposure-Ni(110)
surface covered with dehydrogenated ethylene; T=260°C.

Figure 6. Carbon AES, oxygen AES and CO mass spectrometer signal vs.
time during exposure to oxygen-Ni(110) surface covered with
dehydrogenated ethylene; T=260°C.

Figure 7. $\log \frac{[C]}{[C]_0}$ and $\log \frac{[CO]}{[CO]_0}$ vs. time during exposure to oxygen-Ni(110)
surface covered with dehydrogenated ethylene; T=260°C.

FIG. 1

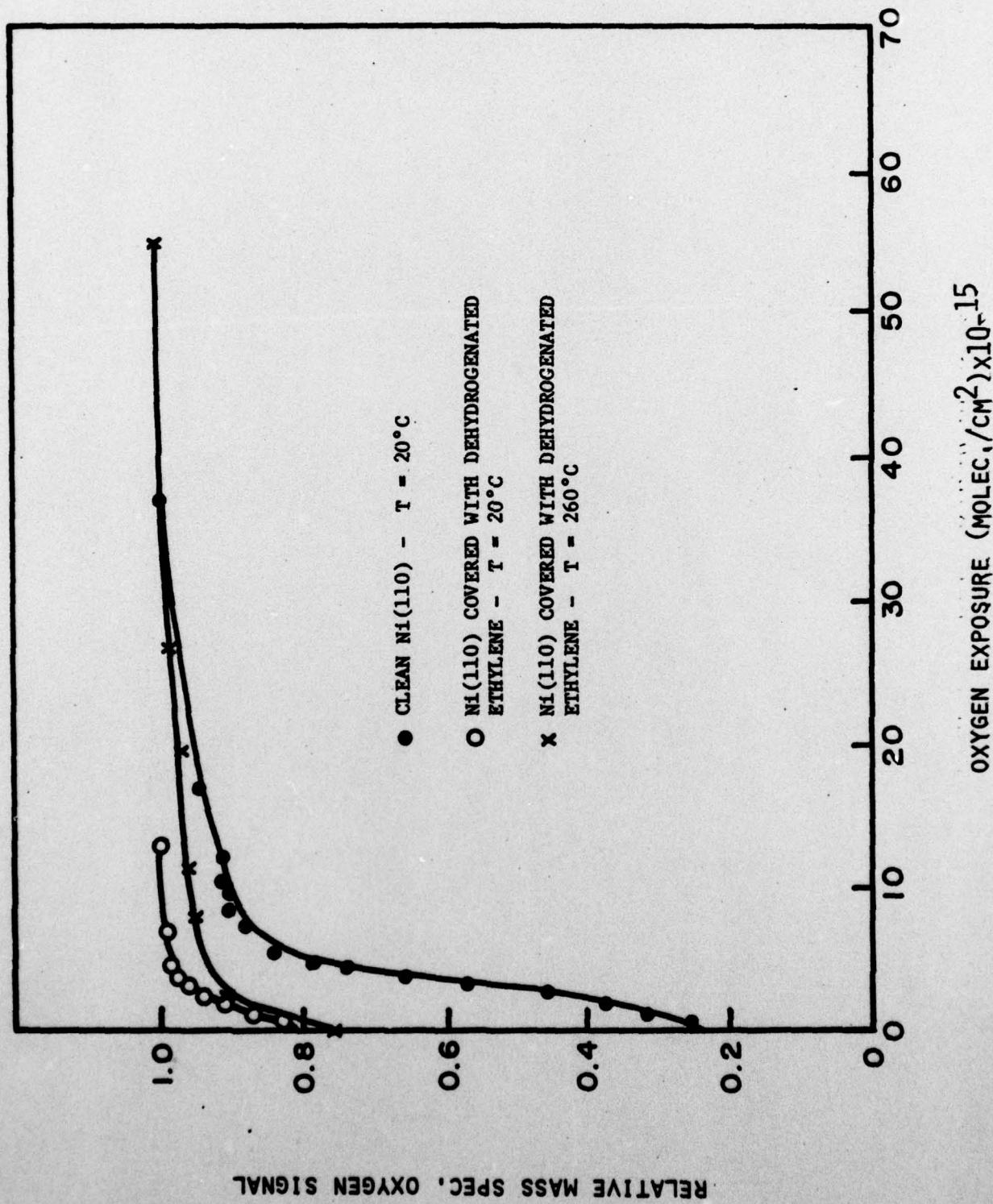


FIG. 2

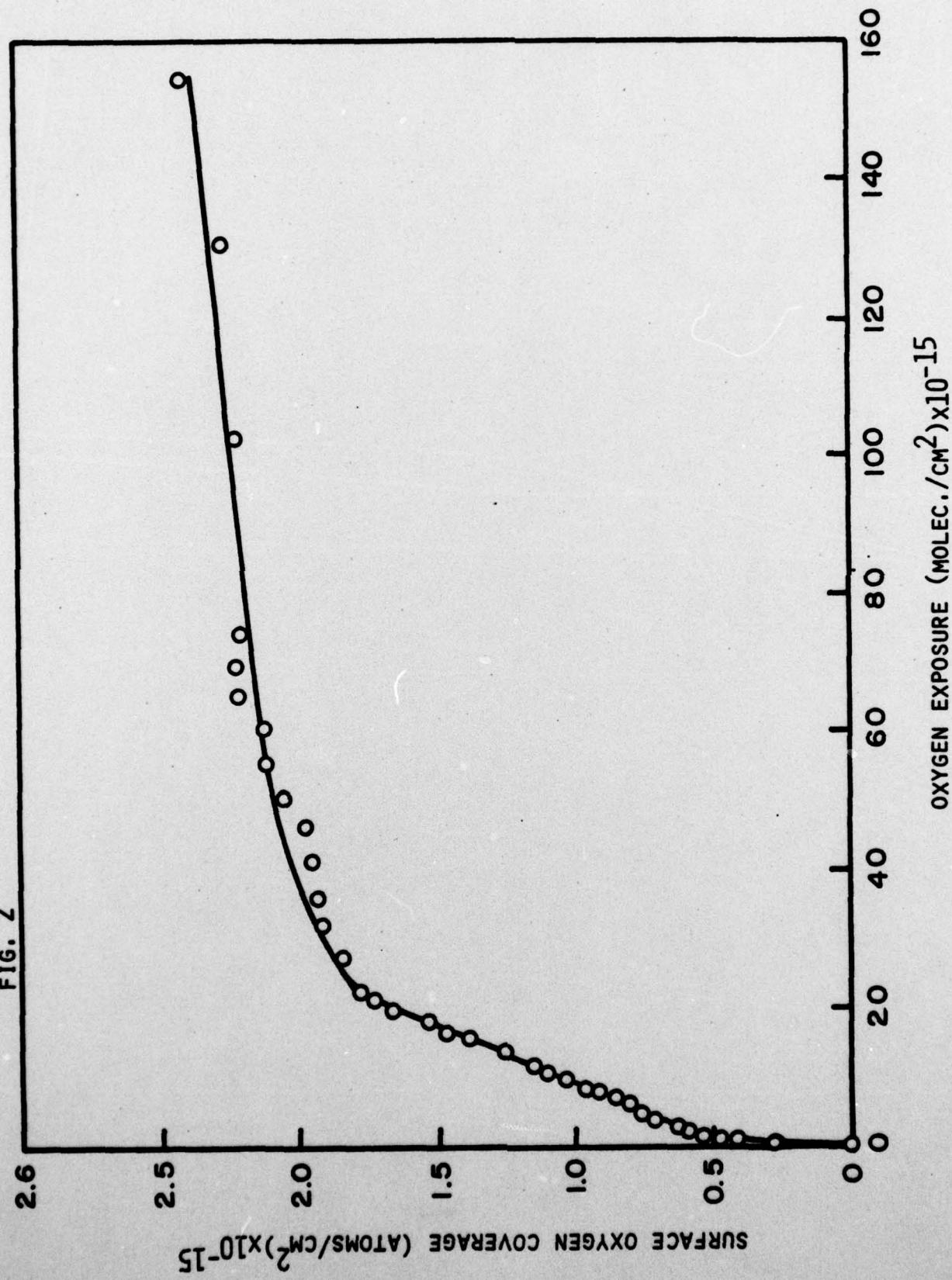


FIG. 3

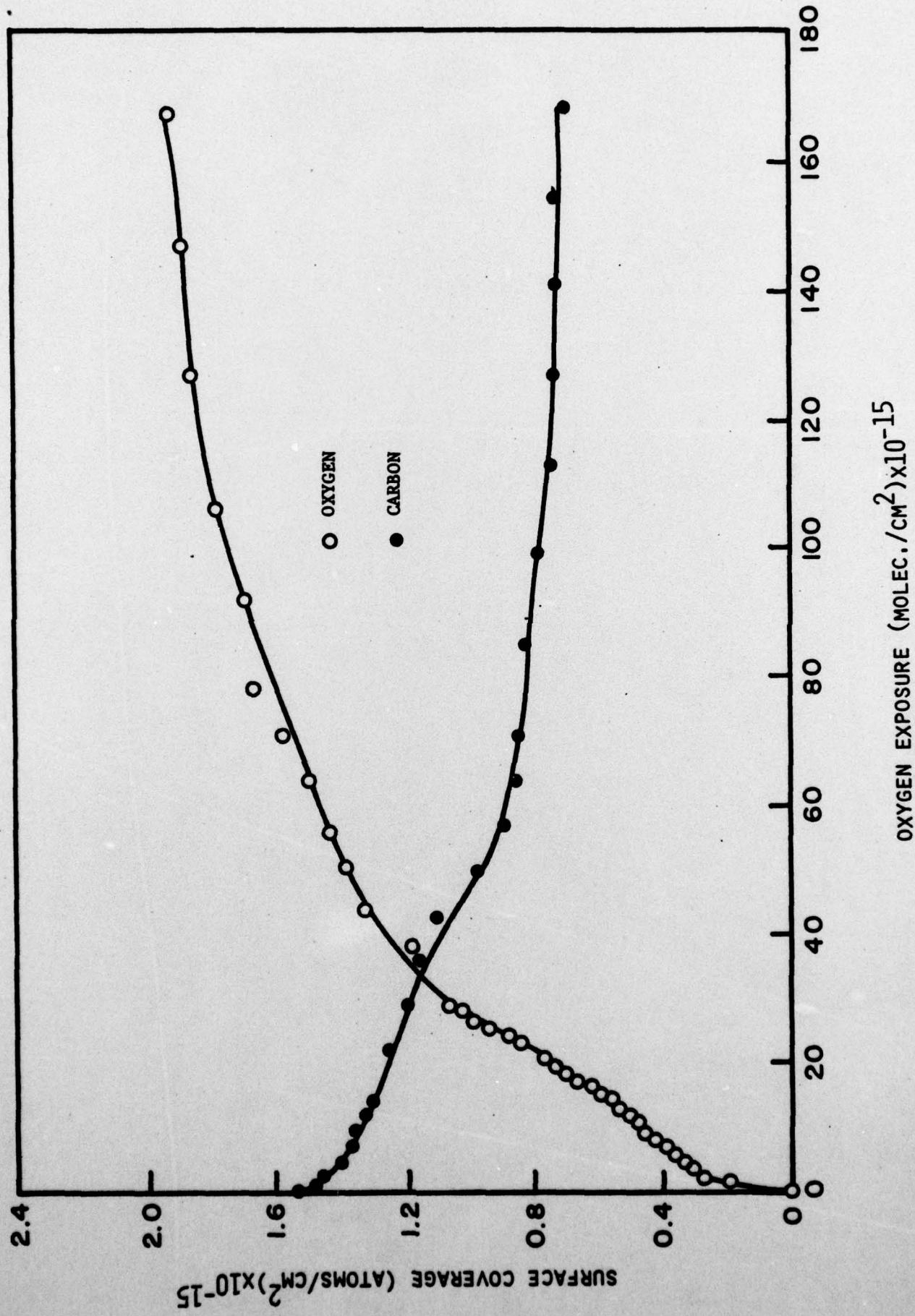


FIG. 4

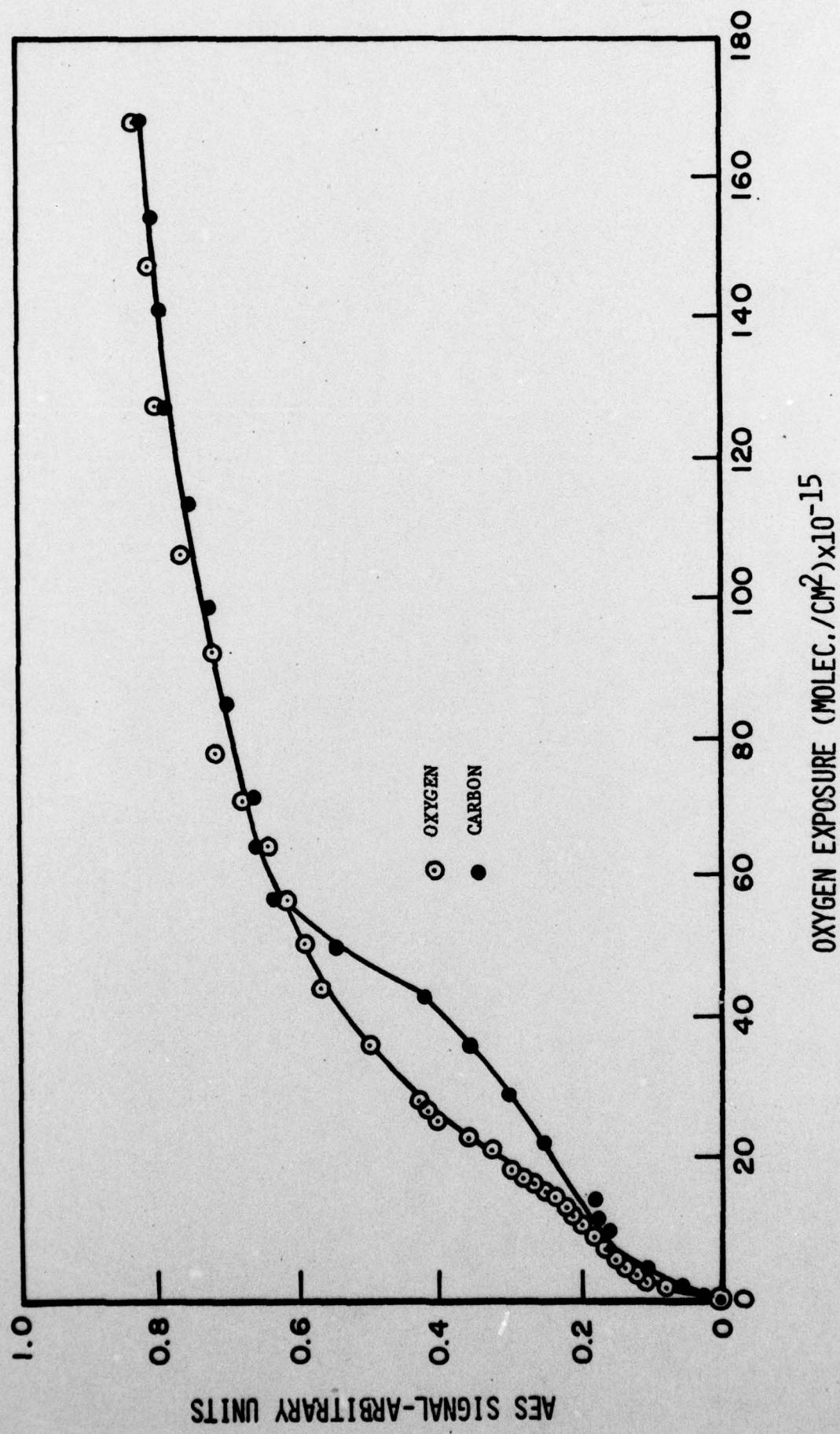


FIG. 5

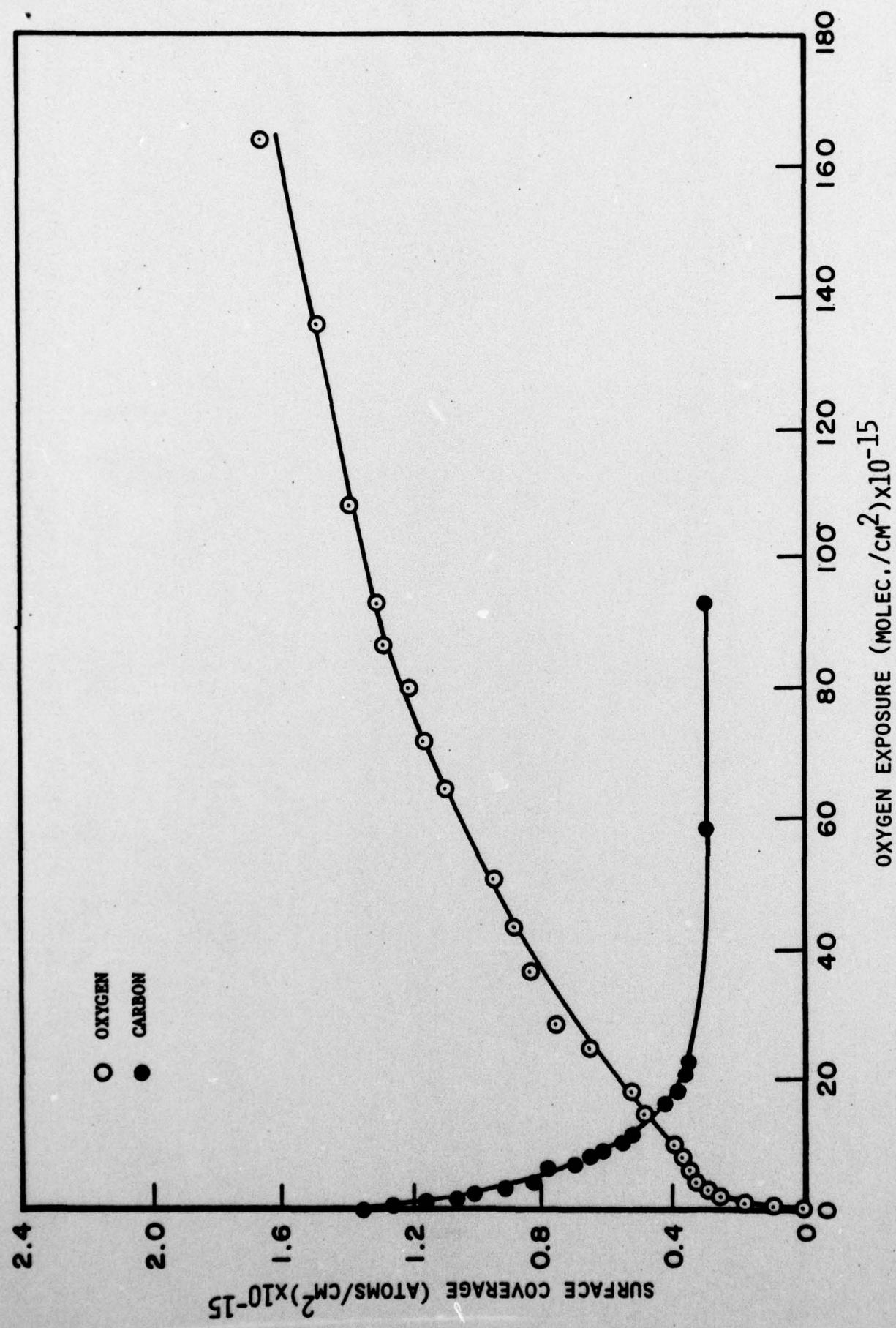


FIG. 6

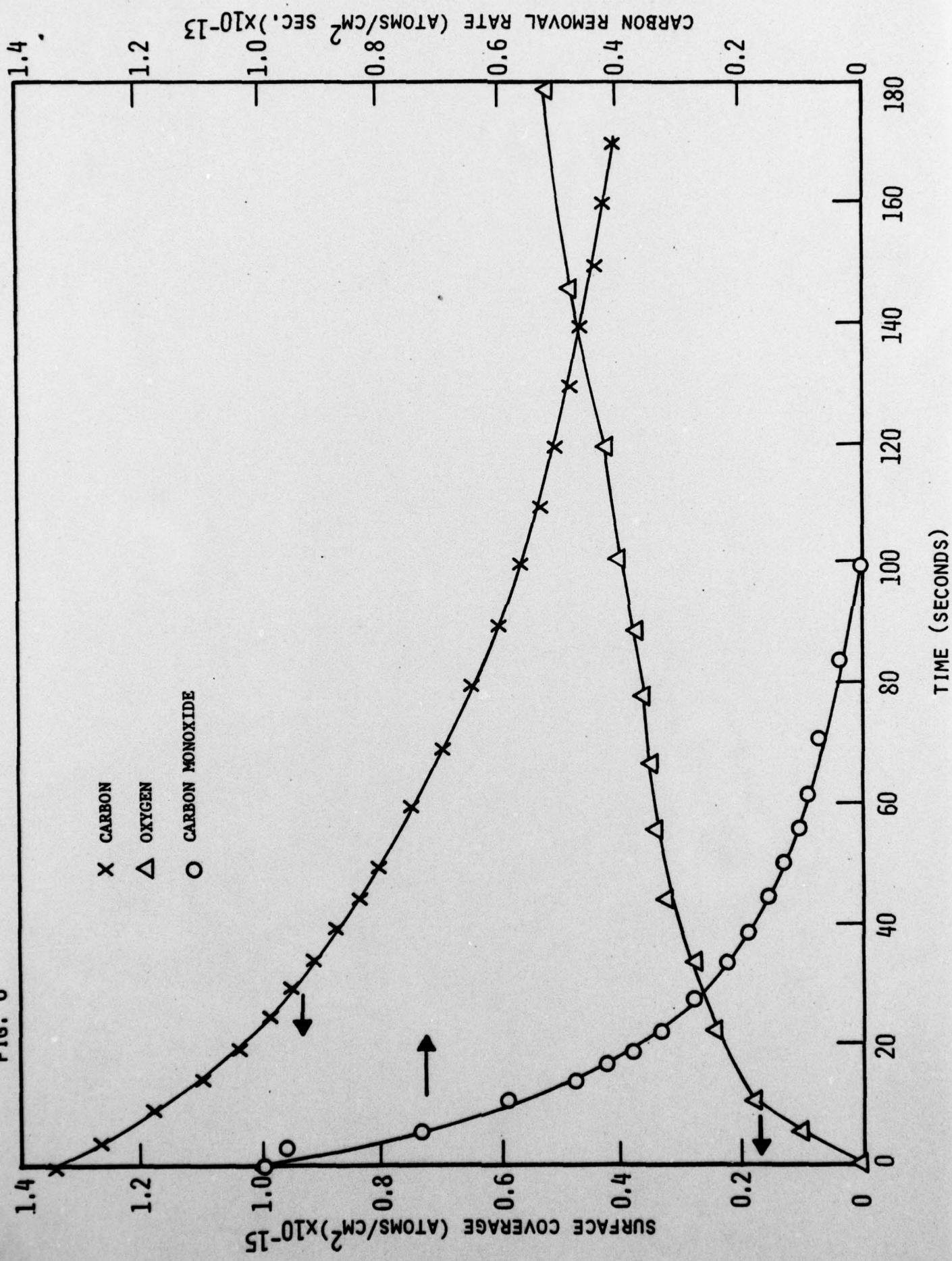


FIG. 7

